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Spin–orbit effect on the magnetic shielding constant: niobium hexahalides and titanium tetrahalides

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Abstract

The ^{93}Nb and ^{47}Ti NMR chemical shifts of niobium hexahalides and titanium tetrahalides are studied theoretically by the ab initio UHF/finite perturbation method including the spin–orbit (SO) interaction. The calculated chemical shifts agree well with experiment for both the Nb and Ti compounds. In contrast to the halides of main-group elements studied previously, the SO effect is generally small for early transition metal halides. The origin of the chemical shifts lies in the d-orbital contribution of the paramagnetic term and is due to the d–d* excitation mechanism. Soft d-orbitals adsorb the SO effect, leaving only a small net spin-orbit effect. The chemical shift shows a monotonic downfield shift as the halogen ligand becomes heavier (inverse halogen dependence), in contrast to the normal halogen dependence observed for the halides of main-group elements. It is expected that such a result is common to other transition metal halides in which the transition metal atom has an open d subshell. © 1997 Elsevier Science B.V.

1. Introduction

The NMR chemical shift is a property which sensitively reflects the change in the valence electronic structure of molecules [1–8]. In recent years, a series of theoretical studies on metal NMR chemical shifts have been carried out in our laboratory [7–28]. These studies enabled us to elucidate the electronic origin of the chemical shifts of various metal complexes: the origin and the mechanism of the chemical shifts are an intrinsic property of the metal atom itself and are therefore closely related with the position of the metal in the periodic table. Several distinct mechanisms have been clarified so far [7].

In a previous paper of this series [21], we formulated the spin–orbit (SO) unrestricted Hartree–Fock (UHF) method, a useful method for calculating the SO effect using the UHF wavefunction, and applied it to calculating the magnetic shielding constant using the finite perturbation (FP) method. A method for the use of effective core potentials (ECPs) including the SO effect in the framework of the SO-UHF/FP method has also been introduced [23]. Our studies have shown that for the halides of main-group elements in which the metal atom has s^2p^n configuration, the SO effect is important. The experimental trends in the NMR chemical shifts of the halogen complexes of ^{1}H, ^{13}C [21], ^{71}Ga, ^{115}In [22], ^{29}Si [23], ^{27}Al [24] and ^{119}Sn [25] could be reproduced only when the SO effects of the ligands were included. Further studies have shown that for the magnetic shielding constants of heavy elements, especially the

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fifth-row elements such as in Hg [26] and W [27], not only the SO effect but also the spin-free relativistic (SFR) effect [28] as well as the coupling between the SO and SFR terms are also important. In this Letter, we examine the influence of the SO interaction on the magnetic constant of the transition metal compound.

Nb and Ti are early transition-metal elements and have open d subshells, $4d^4 5s^1$ and $3d^2 4s^2$, respectively. We studied previously the chemical shifts of some Nb and Ti complexes [19,20] using the RHF/FP method without the SO effect. Our theoretical analyses revealed that the Ti [19] and Nb [20] chemical shifts originate from the d–d* excitation mechanism and that the critical factor is a variation in the d–d* excitation energy ΔE in the sense of second-order perturbation theory.

The NMR chemical shifts of the transition metal elements show some different characteristics from those of the main group elements. The electronic mechanism of the chemical shift is the d–d* excitation mechanism for the transition metal elements, while it is the p-electron and p-hole mechanisms for the main group atoms with s^2p^n configurations [7]. Another main difference is that, for most of the main group elements, the chemical shifts show a higher field shift (normal halogen dependence (NHD)) when the halogen is substituted from Cl to I, and so-called U-shaped relationships exist in most cases. The origin of the NHD was shown to be the SO effect of the halogen ligands [21–27] and that of the U-shaped relationship was clarified previously [7,12,23,24]. However, for transition metal halides only monotonic downfield shifts exist in all the cases studied so far [7,17–20].

In this Letter, we investigate the influence of the SO interaction in niobium hexahalides $NbCl_5X^-$, NbX_6^- (X = F, Cl, Br and I) and titanium tetrahalides TiX_4 (X = Cl, Br and I). We are interested in how important the SO effect is for transition metal halides such as niobium hexahalides and titanium tetrahalides, since the origin and the electronic mechanism of the chemical shifts are largely different between the two kinds of halides.

2. Method of calculation

The Nb and Ti magnetic shielding constants σ are calculated by the SO-UHF/FP method [21]. The chemical shifts δ are calculated using $NbCl_6^-$ and $TiCl_4$ as reference compounds.

The basis set for Nb is the (16s10p7d)/[7s5p4d] set of Huzinaga et al. [29] and the valence orbitals are augmented by p-FOBFs (first-order higher angular momentum basis functions) [15]. The basis set for Ti is (14s8p5d)/[6s4p2d] and the valance orbitals are augmented by p- and d-FOBFs [15]. For the halogen atoms, the core electrons are replaced by relativistic effective core potentials (ECPs) [30–32], and valence double-zeta sets plus p- and d-FOBFs are used; namely, the (4s4p)/[2s2p] set plus p- and d-FOBFs are used for F and Cl [30], the (3s3p)/[2s2p] set plus p- and d-FOBFs for Br [31] and I [32]. For hydrogen, the (4s)/[2s] set of Huzinaga–Dunning [33] plus p FOBFs are used. These

Table 1
Geometries of NbX_6^-, $NbCl_5X^-$ and TiX_4 (X = H, F, Cl, Br and I) used in the present study

	Bond length (Å)							
	NbH_6^-	NbF_6^-	$NbCl_5F^-$	$NbCl_6^-$	$NbCl_5Br^-$	$NbCl_5I^-$	$NbBr_6^-$	NbI_6^-
Nb–Cl [a]			2.434	2.428	2.429	2.428		
Nb–X [a]	1.8755	1.926	1.902		2.586	2.824	2.585	2.824
Ti–X [b]	Ti–H	Ti–Cl	Ti–Br	Ti–I				
	1.6734	2.170	2.339	2.546				

[a] Bond angles are assumed to be 90° and all the bond distances are optimized by the UHF method.

[b] T_d symmetry. The experimental bond distances are taken from Refs. [34,35]. For TiH_4, the experimental value is not available and an optimized geometry at the UHF level is used instead.

basis sets are the same as those used previously [23–25]. It has been shown that by adding the FOBFs to the atoms neighboring the resonant atom the basis set dependence and the gauge origin dependence are decreased [15,16].

The geometries of the niobium halides are assumed to be octahedral or pseudooctahedral, and all the bond distances are optimized by the UHF method with the basis sets as shown above, except that the FOBFs were not included. For titanium tetrahalides, the experimental Ti–X distances [34,35] with T_d symmetry are used. The geometrical parameters used in this Letter are summarized in Table 1.

3. Results and discussion

Figs. 1 and 2 show the Nb and Ti chemical shifts in niobium hexahalides and titanium tetrahalides. The open circle (○) and closed triangle (▲) indicate the values calculated without and with the SO interaction, respectively. The experimental chemical shifts are taken from Refs. [1–6]. In order to examine the SO effects on the Nb and Ti atoms, the SO interactions in NbH_6^- and TiH_4 compounds are investigated. The differences between the calculations with and without SO effects are 35 ppm for NbH_6^- and 41 ppm for TiH_4, in comparison with 8.85 ppm for SnH_4 [25]. Since the SO effect on H is negligible, these values are attributed to the SO effect on the Nb and Ti atoms. These values are also small compared with the order of the chemical shift: 5000 ppm for niobium hexahalides and 2000 ppm for titanium tetrahalides. Therefore, the SO interactions in the Nb and Ti atoms are not considered for the chemical shift calculations given below.

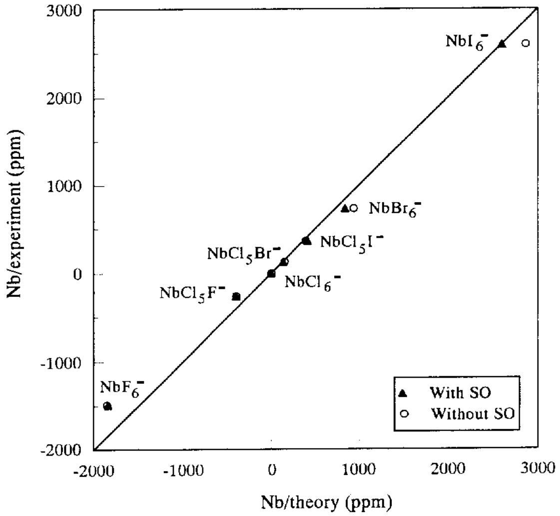

Fig. 1. Correlation between theory and experiment for the chemical shifts of niobium hexahalides. No experimental value is available for NbI_6^-. Therefore, we give only the theoretical values, assuming that the theoretical value with the SO effect appropriately represents the experimental value.

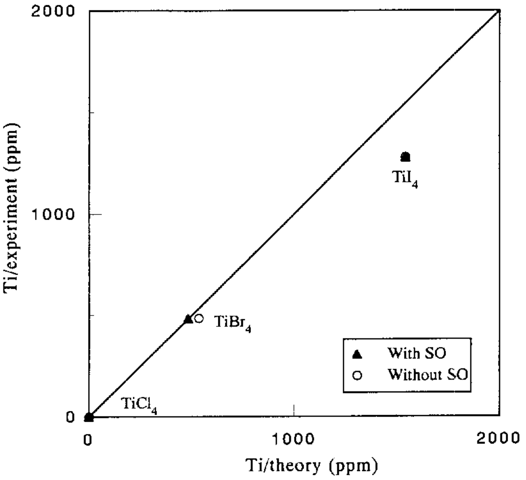

Fig. 2. Correlation between theory and experiment for the chemical shifts of titanium tetrahalides.

Table 2 shows a detailed comparison of the values calculated without and with the SO interaction. The magnetic shielding constants including the SO interaction are divided into the diamagnetic term, paramagnetic term, spin–dipolar term (SD) and Fermi contact (FC) term [21]. The results without the SO effect are different from those reported previously [19,20], but the present results should be more reliable for the better quality of the basis set used.

One particular feature of the results shown in Figs. 1 and 2 is that the influences of the SO interaction on the chemical shifts of niobium hexahalides and titanium tetrahalides are all small; only a little better agreement with the experimental values were obtained by including the SO interaction. This is in marked contrast to the results obtained previously for the main group elements [21–25]. We find

Table 2
Magnetic shielding constants σ and chemical shifts δ of niobium hexahalides and titanium tetrahalides with and without the spin–orbit effect (ppm)

Compound	Without SO				With SO						δ^{expt}
	σ^{dia}	σ^{para}	σ^{total}	δ^{calc}	σ^{dia}	σ^{para}	δ^{SO}(SD)	σ^{SO}(FC)	σ^{total}	δ^{calc}	
NbF_6^-	4067.93	−2037.35	2030.58	−1850.84	4067.93	−2036.65	−0.39	−1.74	2029.15	−1838.46	−1490
$NbCl_5F^-$	4032.07	−3450.72	581.35	−401.61	4032.07	−3449.60	−2.29	9.13	589.31	−398.62	−258
$NbCl_6^-$	4024.96	−3845.22	179.74	0.0	4024.96	−3843.57	−2.59	11.89	190.69	0.0	0
$NbCl_5Br^-$	4023.31	−3993.54	29.77	149.97	4023.31	−3996.63	−6.76	34.09	54.01	136.68	129
$NbCl_5I^-$	4021.15	−4233.55	−212.40	392.14	4021.15	−4284.04	−23.92	62.28	−224.52	415.21	365
$NbBr_6^-$	4015.27	−4775.20	−759.93	939.57	4015.28	−4785.50	−21.46	138.09	−653.59	844.28	737
NbI_6^-	4002.44	−6684.67	−2682.23	2861.97	4002.48	−6902.0	−85.81	576.73	−2408.60	2599.29	...
$TiCl_4$	1738.41	−2094.97	−356.56	0.0	1738.41	−2092.61	−2.37	5.17	−351.20	0.0	0
$TiBr_4$	1729.59	−2609.29	−879.70	532.14	1729.59	−2623.68	−15.70	78.52	−831.27	480.07	483
TiI_4	1720.92	−3621.07	−1900.15	1543.59	1720.93	−4115.96	−21.61	517.37	−1899.01	1547.81	1278

in Table 2 that the SO effect indeed increases as the halogen ligand becomes heavier, as in $NbBr_6^-$ and NbI_6^-. For NbI_6^-, the chemical shifts without and with the SO effect are calculated to be 2862 and 2599 ppm, respectively, showing a larger SO effect as expected for the compounds containing multiple I atoms. Unfortunately, there is no experimental value available for comparison with the present theoretical value. For all the niobium hexahalides studied here, a better agreement with the experimental values is obtained by including the SO interaction though the SO effect is small. In comparison with niobium hexahalides, the net SO effect for titanium tetrahalides is much smaller.

The FC and the SD terms originate from the SO interaction. Table 2 shows that the FC term is dominant in the SO effect and leads the chemical shift to higher field; the same trend has been observed for all the compounds studied previously in our laboratory [21–27]. For the halides of main group elements, the SO effect was the origin of the chemical shifts and caused the NHD observed for these halides. However, for the transition metal halides studied here, the paramagnetic term also changes greatly when the SO effect is taken into account, showing a larger coupling between them. This means that the paramagnetic term is also sensitive to the SO effect. The smallness of the net SO effect for the chemical shifts is due to the cancellation between the SO and paramagnetic terms. The sign of the effect of the SO effect on the paramagnetic term, $\Delta\sigma^{\text{para}}$ is different from that of $\Delta\sigma^{\text{SO}}$, which is $\Delta\sigma^{\text{FC}}$ plus $\Delta\sigma^{\text{SD}}$; the SO effect causes a higher field shift, while the paramagnetic term causes a lower field shift. This is the case especially for TiI_4, in which the SO effect causes a higher field shift of about 500 ppm, a large value, while the paramagnetic term causes an inverse lower field shift of about 500 ppm, leaving the net chemical shift totally unchanged. This cancellation is interestingly less incomplete in $TiBr_4$, so that the SO effect shown in Fig. 2 is larger for $TiBr_4$ than for TiI_4. The diamagnetic terms with and without the

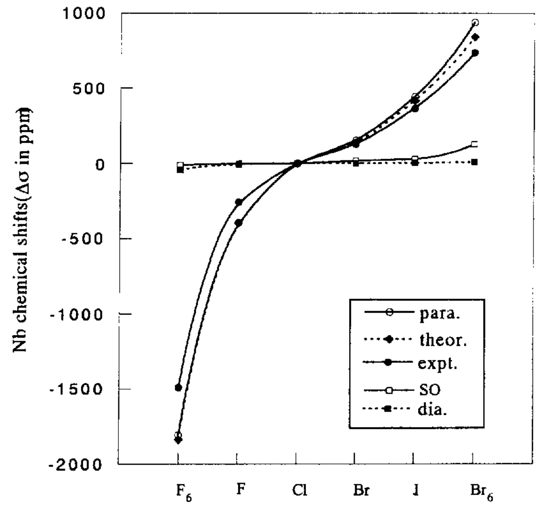

Fig. 3. Dependence of the Nb chemical shift and the diamagnetic, paramagnetic, spin–dipolar and Fermi contact contributions in NbX_6^- and $NbCl_5X^-$ (X = F, Cl, Br and I).

Table 3
MO contributions in diamagnetic, paramagnetic, spin-dipolar and Fermi contact terms of niobium hexahalides and titanium tetrahalides (ppm)

Compounds	σ^{dia}		σ^{para}		σ^{SO} (SD)		σ^{SO} (FC)		σ^{total}	δ^{calc}	δ^{expt}
	core	valence	core	valence	core	valence	core	valence			
NbF_6^-	3810.48	257.45	−1407.85	−628.80	−0.64	0.25	−2.24	0.50	2029.15	−1838.46	−1490
$NbCl_5F^-$	3816.39	215.68	−239.75	−3209.85	0.98	−3.26	−10.64	19.77	589.31	−398.62	−258
$NbCl_6^-$	3818.01	206.95	432.02	−4275.59	1.50	−4.09	−13.82	25.71	190.69	0.0	0
$NbCl_5Br^-$	3818.01	205.30	449.21	−4445.84	3.72	−10.49	−32.83	66.92	54.01	136.68	129
$NbCl_5I^-$	3817.96	203.20	476.97	−4761.01	11.93	−35.85	−103.92	166.20	−224.52	415.21	365
$NbBr_6^-$	3818.10	197.18	562.52	−5348.02	14.92	−36.38	−130.92	269.01	−653.59	844.28	737
NbI_6^-	3818.04	184.44	835.93	−7737.93	67.91	−153.72	−694.24	1270.97	−2408.6	2599.29	···
$TiCl_4$	1579.84	158.57	191.16	−2283.77	−0.51	−1.86	−8.85	14.22	−351.20	0.0	0
$TiBr_4$	1580.18	149.42	256.19	−2879.87	−3.91	−11.79	−112.15	190.67	−831.27	480.07	483
TiI_4	1580.37	140.56	405.86	−4521.82	−16.23	−5.12	−881.94	1399.31	−1899.01	1547.81	1278

SO effect are essentially the same, showing that the diamagnetic term is insensitive to the SO interaction, which is natural since the diamagnetic term reflects the structural factor of the compound [7].

Fig. 3 shows the contributions of the diamagnetic term, paramagnetic term and SO term to the chemical shifts in niobium hexahalides. It is clearly shown that the contributions of the diamagnetic term and the SO term are small. The chemical shift of niobium hexahalides is due to the dominant contribution of the paramagnetic term. This agrees with a previous study on the Nb chemical shift [20], showing that it is due to the d–d* excitation mechanism.

Next, we study the MO and AO contributions to the chemical shifts of niobium hexahalides and titanium tetrahalides. The definitions of the MO and AO contributions were given in Ref. [8]. Table 3 shows the element of the magnetic shielding constant partitioned into the core and valence MO contributions, and Table 4 shows the partitioning into the metal AO and ligand contributions. For comparison, the metal AO and ligand contributions of the chemical shifts without the SO interaction are shown in Table 5. Table 3 shows that the variations in the core–orbital contributions are small in all the diamagnetic, paramagnetic, SD and FC terms, while the valence-orbital contributions determine the trends of all the terms. Table 4 shows that the diamagnetic term is mainly determined by the ligand contributions as expected [7–9], while for σ^{para}, σ^{SO} (SD) and σ^{SO}

Table 4
AO contributions in diamagnetic, paramagnetic, spin–dipolar and Fermi contact terms of niobium hexahalides and titanium tetrahalides (ppm) with SO interaction

Compound	σ^{dia}		σ^{para}			σ^{SO}(SD)				σ^{SO}(FC)		δ^{calc}	δ^{expt}
	metal	ligand	p	d	ligand	s	p	d	ligand	s	ligand		
NbF_6^-	3837.12	230.81	−677.32	−1124.30	−235.01	−0.02	0.17	−0.67	0.03	−1.88	0.14	−1838.46	−1490
$NbCl_5F^-$	3847.53	184.54	−751.29	−2516.41	−181.90	0.07	0.34	−2.67	−0.04	9.11	0.02	−398.62	−258
$NbCl_6^-$	3850.20	174.76	−723.99	−2946.42	−173.90	0.11	0.54	−3.18	−0.06	11.96	−0.07	0.0	0
$NbCl_5Br^-$	3851.46	171.85	−708.95	−3120.21	−167.47	0.72	1.24	−8.37	−0.35	34.78	−0.69	136.68	129
$NbCl_5I^-$	3851.73	169.42	−679.73	−3442.11	−162.20	1.26	2.67	−26.69	−1.16	65.77	−3.49	415.21	365
$NbBr_6^-$	3860.65	154.63	−622.65	−4025.27	−137.59	2.81	5.75	−28.31	−1.71	142.49	−4.41	844.28	737
NbI_6^-	3857.70	144.78	−363.71	−6424.24	−114.05	4.88	28.53	−116.69	−2.53	582.44	−5.71	2599.29	···
$TiCl_4$	1608.60	129.81	−658.51	−1289.71	−144.40	−0.02	−2.01	−0.40	0.06	5.73	−0.36	0.0	0
$TiBr_4$	1612.79	116.80	−689.14	−1812.34	−122.20	2.63	−14.12	−3.59	−0.63	79.76	−1.24	480.07	483
TiI_4	1609.82	111.11	−810.40	−3196.27	−109.29	2.62	−40.54	20.16	−3.60	524.81	−7.43	1547.81	1278

Table 5
AO contributions in diamagnetic, paramagnetic terms of niobium hexahalides and titanium tetrahalides (ppm) without SO interaction

Compound	σ^{dia}		σ^{para}			δ^{calc}	δ^{expt}
	metal	ligand	p	d	ligand		
NbF_6^-	3837.12	230.81	−677.40	−1124.93	−235.01	−1850.84	−1490
$NbCl_5F^-$	3847.53	184.54	−751.27	−2516.54	−181.90	−401.61	−258
$NbCl_6^-$	3850.20	174.76	−723.92	−2948.14	−173.16	0.0	0
$NbCl_5Br^-$	3851.46	171.85	−709.05	−3116.97	−167.52	149.97	129
$NbCl_5I^-$	3851.72	169.43	−682.68	−3388.17	−162.20	392.14	365
$NbBr_6^-$	3860.63	154.64	−621.79	−4015.72	−137.69	939.57	737
NbI_6^-	3857.76	144.68	−365.42	−6204.10	−115.15	2861.97	···
$TiCl_4$	1608.60	129.81	−658.95	−1291.61	−144.41	0.0	0
$TiBr_4$	1612.79	116.80	−688.68	−1798.33	−122.29	532.14	483
TiI_4	1609.82	111.11	−777.44	−2733.12	−109.29	1543.59	1278

(FC), the ligand AO contributions are small. For the FC term, the metal s AO contribution is dominant, and for the paramagnetic term, the metal d AO contribution is important. From the results with and without the SO interaction shown in Tables 4 and 5, respectively, it is clear that the difference mainly comes from the metal d-orbital contribution. The d-orbital contribution of the paramagnetic term by including the SO effect increases by 220 ppm for NbI_6^- and 460 ppm for TiI_4, which cancels the direct SO effect, resulting in a net small SO effect.

Fig. 4 shows the dependence of the Nb paramagnetic shielding constants and their p and d components. The variations in the p AO contribution are quite small, and the variations in the d orbital contributions determine the changes in the paramagnetic term. Therefore, for σ^{para} of Nb, the d-orbital contribution is evidently the most significant. Similar results are also found for titanium tetrahalides. This is in accordance with our previous finding that the Nb and Ti chemical shifts are due to the d–d* excitation mechanism [19,20].

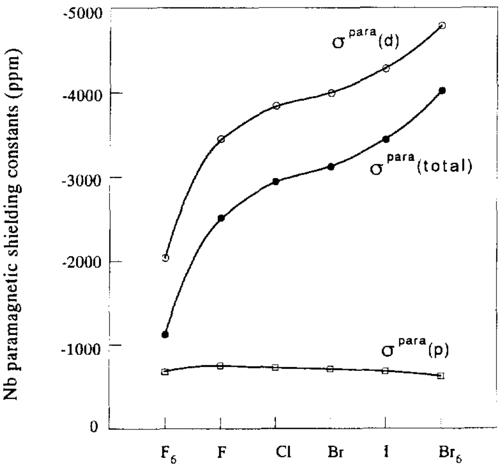

Fig. 4. Nb paramagnetic term and the p- and d-orbital contributions in NbX_6^- and $NbCl_5X^-$ (X = F, Cl, Br and I).

Let us compare the different SO effects between the main group element halides and the transition metal halides. The former has p^n configuration, while the latter has d^n configuration. We have shown previously [7] that for the main group elements, the p AO contribution to the chemical shifts is dominant. The U-shaped dependence for some main group elements is due to the IHD (inverse halogen dependence) for F and Cl and the NHD for Cl, Br and I as shown for silicon [23] and aluminum [24] tetrahalides. The IHD is due to the electronegativity difference of the ligands [12] and the NHD is due to the SO effect. On the other hand, for transition metal halides, the chemical shift originates from the d-orbital contribution, which arises from the d–d* mechanism as clearly shown for Mo [17,18] and Nb [20] complexes. It arises from the open d-subshell nature of transition metal complexes. Unlike the main group elements, the chemical shifts of the transition metal halides show only the monotonic lower field shift as the halogen ligand becomes heavier. This lower field shift is explained by the d-orbital contribution to the paramagnetic term. The SO effect causes a higher field shift, but is compensated by the paramagnetic term. The d-orbitals of the transition metals are much softer than the p-orbitals of the main group element, so that the spin–orbit effect is somewhat 'absorbed' by the change in the d-orbital contribution. The net SO effect is small in transition metal halides. The different electronic origins of the chemical shifts cause different SO effects. We expect that the small SO effect found here for the Ti and Nb compounds is common to the other transition metal halides which contain open d subshells.

4. Conclusions

In this Letter, we have investigated the SO effect in the Nb and Ti chemical shifts of niobium hexahalides and titanium tetrahalides by the SO-UHF/FP method [21]. The SO interaction is calculated using the effective SO potential [23].

(1) The origin of the chemical shifts lies in the change of the paramagnetic term of the shielding constant. The d-orbital contribution is dominant. The monotonic downfield shift is due to the monotonic change in the paramagnetic term, when the halogen is substituted from F to I.

(2) The SO effect is small for the Nb and Ti chemical shifts, though the calculated results are improved by including the SO effect. The SO term itself is not small, but the paramagnetic term is also sensitive to the SO effect and they cancel each other, leaving a generally small net SO effect. The FC term is dominant in the SO effect as shown for the halides of main group metals.

(3) The evidently different SO effects between the halides of main group elements and transition metals are due to the different electronic mechanisms of the chemical shifts. The chemical shifts of main group element halides is due to the p-electron mechanism while that of transition metal halides is due to the d-electron mechanism. The d orbitals of transition metals are much softer than the p orbitals of main-group elements, so that the spin–orbit effect is somewhat 'absorbed' by the change in the d-orbital contribution of the paramagnetic term. This is the reason why the net SO effect is small for the transition metal halides.

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